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(54) Title: <b>MELT POLYMERIZATION PROCESS FOR MAKING POLYURETHANES</b>			
<pre> graph LR     A[A] --&gt; FEED[FEED ZONE]     B[B] --&gt; FEED     C[C] --&gt; FEED     FEED --&gt; MIX[SINGLE HIGH SHEAR MIXING ZONE]     MIX --&gt; EXTR[EXTRUSION ZONE]     EXTR --&gt; COL[PRODUCT COLLECTION ZONE]     </pre>			
(57) Abstract			
<p>Disclosed is an improved reactive extrusion process for the continuous preparation of a hard polyurethane having <math>T_g</math> values greater than 80°C. The polyisocyanate and polyol ingredients are reacted in a twin-screw extruder which is limited to a single zone of high shear mixing. The present process prevents the formation of small bubbles in the extruded polyurethanes as well as the formation of yellow coloration in what should be an essentially water white polymer, problems which are encountered in the preparation of these hard polyurethanes using the prior art processes wherein the high shear mixing is carried out in multiple zones.</p>			

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## MELT POLYMERIZATION PROCESS FOR MAKING POLYURETHANES

This invention relates to polyurethanes and is more particularly concerned with a process for the preparation of high flexural modulus polyurethane plastics by reactive extrusion.

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U.S. Patents 4,376,834, 4,567,236, and 4,822,827 introduced novel classes of both thermoset and thermoplastic polyurethane polymers to the plastics molding art. These materials are characterized by high impact resistance, stiffness, and other structural strength properties similar to nylon and other engineering thermoplastics. Additionally, some members of this group of new materials have exceptionally high T<sub>g</sub> values, as high as 165°C. The advent of these materials has provided the molding industry with excellent alternative engineering thermoplastic material choices. Notably, some of these polyurethanes are thermoplastic and contain little or no soft segment because of either the very minor amount, or, complete absence, of high molecular weight polyol in their formulations. Because of their thermoplastic nature and, similarly, to the well known softer thermoplastic polyurethanes, these materials lend themselves to manufacture by the reactive

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extrusion process. This method is preferable because of its economic advantages in terms of simply adding the necessary ingredients into a screw extruder in the absence of solvents and continuously, but rapidly, producing a finished product in the form of desirable profiles or pellets. Such continuous methods are preferably carried out in multi-shaft screw extruders, more preferably twin-screw extruders.

U.S. Patent 3,642,964 and its German counterpart DE 2059570 were the first disclosures to the continuous reactive extrusion of soft thermoplastic polyurethanes in twin-screw extruders. This teaching called for high shear mixing zones in the extruder barrel with each zone having a series of kneading blocks which can have various configurations. More than one such mixing zone or series of blocks is employed on each of the twin-screw shafts. The plurality of mixing zones are either separated by conveying screws or else connected as one long multi-zone depending on the manufacturer's design of the extruder. It will be obvious to one skilled in the art that such extruders must also be equipped with the conventional conveyor screws both in respect of a feed zone and metering zone both before and/or after the mixing zones. Additional types of screws may be employed such as, for example, those which cause backward flow in order to keep mixing zones filled. This process works admirably with soft thermoplastic polyurethanes falling in the hardness range of 60 Shore A to 75 Shore D.

U.S. Patent 3,963,679 discloses a process quite similar to the one described above in employing the extrusion apparatus set forth in Figure 1 of its

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disclosure. Primarily, this method differs from that of U.S. Patent 3,642,964 supra in requiring that the polyurethane forming mixture be subjected to its first high shear mixing during the time it has a viscosity of 10,000 to 100,000 centipoise (10 to 100 Pa-s). This limitation is paramount to the invention disclosed because when only a single kneading zone is employed after the viscosity has surpassed the upper viscosity limit (Example 1b, column 14) the product was inhomogeneous. Similarly, when two zones are employed (Example 1c, lines 28 to 38) the product polyurethane is inhomogeneous. Delaying the reaction until the first zone is reached results in the process of the invention as described *loc cit*, lines 40 to 45. This reference inherently calls for more than one zone of high shear mixing with the critical limitation being the placement of the first zone to meet the reaction mixture viscosity range set forth above.

Following the above art, there are a number of disclosures to the reactive extrusion method for preparing thermoplastic polyurethanes. U.S. Patent 4,245,081 discloses the continuous preparation using the procedures described in U.S. Patents 3,642,964 and 3,963,679 discussed supra with the inventive step being the use of a mixture of glycol extenders. U.S. Patents 4,261,946 and 4,342,847 each disclose essentially the same process differing only in the component proportions. The former is directed to modifying 70 to 98 parts of a thermoplastic polymer with 2 to 30 parts of polyurethane forming components. The procedure is accomplished by adding the thermoplastic polymer, inclusive of preformed polyurethane, and the polyurethane forming ingredients to the first and second

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inlets respectively of an extruder. The polyurethane formed *in situ* in the extruder is inclusive of both those with and without soft segments. The latter has the preformed thermoplastic polymer at 4 to 65 parts with the polyurethane forming components at 35 to 96 parts. Both patents disclose the use of the same twin-screw technology described in U.S. Patent 3,963,679 *supra*.

U.S. Patent 4,595,709 discloses a method for converting toluene diisocyanate distillation residues to useful polyurethane polyaddition products containing urethane groups by continuously reacting the residues with low molecular weight compounds containing hydroxyl groups. The reaction is carried out in multiple-screw extruders using the extrusion technology of U.S. Patent 3,963,679 cited *supra*.

Now the new classes of polyurethanes set forth in the three patents cited *supra* can be prepared using the twin-screw extruder technology of the prior art discussed above. However, there are problems encountered which appear to be unique to these new high melting materials. One problem is a tendency for gaseous formation or the appearance of small bubbles in the extruded polymer. Another problem is the formation of yellow coloration in what should be an essentially water white polymer. Part of the problem lies with their high melting characteristics and high melt viscosities. It is a known phenomenon that the polymer chains of thermoplastic polyurethanes can unzip, then zip back together during thermal treatment. Generally speaking, this is not a problem with the softer polyurethanes made by the prior art processes discussed above. However, in

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the case of these newer materials, the higher temperature required during processing may be the cause of the difficulties. While not wishing the present invention to be limited by any theoretical considerations but only by the claims appended herein-  
5 below, it is believed that during the unzipping and zipping of the polymer chains at the elevated processing temperatures the reformed isocyanate groups can react with each other to form carbodiimide and evolve carbon  
10 dioxide thus resulting in bubble formation. The yellow coloration appears to arise from some thermally initiated side-reaction either connected to, or, independent of, the above proposed carbon dioxide formation.

15 Accordingly, it would be most desirable to have a continuous reactive extrusion process available which could ensure the preparation of these new polyurethane products without the troublesome side effects noted  
20 above.

The present invention is directed to an improved reactive extrusion process for the continuous  
25 preparation of a polyurethane having a  $T_g$  greater than  $80^\circ\text{C}$  from a reaction mixture comprising a polyisocyanate and at least one polyol component by passing said reaction mixture through a twin-screw extruder having besides the feed zone, zones of high shear mixing and a  
30 metering zone, wherein the improvement comprises limiting the high shear mixing to a single zone.

The polyurethanes prepared in accordance with the present invention are substantially free of bubble formation and, surprisingly, are found to be much

lighter in color than those same chemically constituted polyurethanes but prepared by the prior art method. The difference in color is readily detected by comparing Yellowness Index determinations for the respective samples when measured in accordance with ASTM Test Method D-1925.

Quite unexpectedly, the present reactive extrusion process, if desired, can be carried out at much lower L/D ratios than prior art extrusion methods. The term L/D ratio refers to the overall length of the twin-screw extruder barrel divided by the barrel diameter, usually measured in millimeters (mm). In running at lower L/D ratios which means shorter barrels, this translates to an additional benefit of lowered energy consumption compared with prior art methods.

Accordingly, the process in accordance with the present invention meets the needs set forth above with the added benefit of lower energy consumption.

The polyurethanes produced in accordance with the present process are made up of either all hard segments or hard segments with only a minor proportion of soft segments arising from the small amount of high molecular weight polyol used which is discussed in the art cited supra. They are characterized by the following properties: high impact resistance of at least 1 ft. lb. per inch (53 J/m), preferably at least 3 ft. lbs. per inch (160 J/m) of notch measured by the notched Izod test in accordance with ASTM D256-56; high heat deflection temperature when subjected to a 264 psi (1.82 MPa) flexural load in accordance with ASTM D648-56 of at least 50°C, preferably at least 70°C; high flexural



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modulus of at least about 150,000 psi (1034 MPa) as measured by ASTM D790; T<sub>g</sub> or secondary transition temperature greater than 80°C; and hardness values as measured on the Rockwell hardness range R (as measured by ASTM D785) of greater than 100.

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Additionally, those polyurethanes prepared with non-aromatic polyisocyanates are characterized by having essentially optical clarity and light stability.

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The products produced in accordance with the present invention find utility, for example, in the molding of under the hood auto and truck parts such as distributor covers, filter bowels, air-filter units and covers, containers and covers for electronic circuitry, medical devices requiring transparency and autoclavability, surgical instrument trays and containers for steam sterilization.

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Figure 1 shows in schematic form one typical embodiment of the process of the invention.

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The reactive extrusion process in accordance with the present invention is directed primarily to certain specific classes of hard, high temperature resistant polyurethanes defined above. All of the reactants, components, ingredients, and catalysts and proportions therefor have already been set forth in detail in U.S. Patents 4,376,834; 4,567,236; and 4,822,827. The compositions include both thermoplastic injection-moldable resins and thermoset resins. The latter are obtained when polyisocyanates, extenders and polyols of functionalities greater than two are employed as taught in the previously mentioned patents.

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Thermoplastic products are obtained by employing substantially difunctional polyisocyanates and difunctional extenders and, if used, polyols having functionalities preferably not exceeding about 4. Since the amount by weight of the polyol employed is relatively small, it is thus possible to employ such components having functionalities greater than two without detracting from the thermoplasticity of the polymer. However, the thermoplastic materials are greatly preferred and in this connection the following sets forth some of the more preferred reactants which can be employed.

Illustrative isocyanates but non-limiting thereof are methylenebis(phenyl isocyanate) including the 4,4'-isomer, the 2,4'-isomer and mixtures thereof, m- and p-phenylene diisocyanates, chlorophenylene diisocyanates, α,α'-xylylene diisocyanate, 2,4- and 2,6-toluene diisocyanate and the mixtures of these latter two isomers which are available commercially, tolidine diisocyanate, hexamethylene diisocyanate, 1,5-naphthalene diisocyanate and isophorone diisocyanate; cycloaliphatic diisocyanates such as methylenebis(cyclohexyl isocyanate) including the 4,4'-isomer, the 2,4'-isomer and mixtures thereof, and all the geometric isomers thereof including trans/trans, cis/trans, cis/cis and mixtures thereof, cyclohexylene diisocyanates (1,2-; 1,3-; or 1,4-), 1-methyl-2,5-cyclohexylene diisocyanate, 1-methyl-2,4-cyclohexylene diisocyanate, 1-methyl-2,6-cyclohexylene diisocyanate, 4,4'-isopropylidenebis(cyclohexyl isocyanate), 4,4'-diisocyanatodicyclohexyl, and all geometric isomers and mixtures thereof. Also included are the modified forms of methylenebis(phenyl isocyanate). By the latter are

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meant those forms of methylenebis(phenyl isocyanate) which have been treated to render them stable liquids at ambient temperature (circa 20°C). Such products include those which have been reacted with a minor amount (up to about 0.2 equivalents per equivalent of polyisocyanate) of an aliphatic glycol or a mixture of aliphatic glycols such as the modified methylenebis(phenyl isocyanates) described in U.S. Patents 3,394,164; 3,644,457; 3,883,571; 4,031,026; 4,115,429; 4,118,411; and 4,299,347. The modified methylenebis(phenyl isocyanates) also include those which have been treated so as to convert a minor proportion of the diisocyanate to the corresponding carbodiimide which then interacts with further diisocyanate to form uretone-imine groups, the resulting product being a stable liquid at ambient temperatures as described, for example, in U.S. Patent 3,384,653. Mixtures of any of the above-named polyisocyanates can be employed if desired.

A particularly preferred group of diisocyanates includes aromatic and cycloaliphatic diisocyanates and mixtures thereof as exemplified above. Most preferred species within this group include methylenebis(phenyl isocyanate) including both 4,4'- and 2,4'-isomers and mixtures thereof with 4,4'- preferred, methylenebis-(cyclohexyl isocyanate) including the 4,4'- and 2,4'-isomers and mixtures thereof including all of the geometric isomers thereof with the 4,4'- preferred, and 4,4'-isopropylidenebis(cyclohexyl isocyanate).

The at least one polyol component called for above in its broadest scope will include the chain extender and any polyol if it be employed. In respect of the difunctional extenders, they are not strictly

- limited to hydroxyl-containing extenders but can include other active hydrogen materials such as amine groups or mixtures of such extender types. However, the preferred extenders comprise at least one diol having a molecular weight of from 60 to 400. Included in this group are
- 5 the aliphatic diols having 2 to 10 carbon atoms, inclusive of bis(hydroxyalkyl)cycloalkanes; and the cycloalkane diols described in U.S. Patent 4,822,827 as having 4 to 12 cycloaliphatic carbon atoms.
- 10 Illustrative of such diols are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 1,3-butanediol, 2,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, 1,9-nonanediol, 2-methyloctane-
- 15 -1,8-diol, 1,4-cyclohexanedimethanol, neopentyl glycol, hydroquinone bis(hydroxyethyl)ether, diethylene glycol, dipropylene glycol and tripropylene glycol including mixtures of two or more such diols; 1,2-cyclohexanediol,
- 20 1,3-cyclohexanediol, 1,4-cyclohexanediol, 2-cyclohexene-1,4-diol, 2-methyl-1,4-cyclohexanediol, 2-ethyl-1,4-cyclohexanediol, 1,3-cycloheptanediol, 1,4-cycloheptanediol, 2-methyl-1,4-cycloheptanediol and 4-methyl-1, 3-cycloheptanediol; 4,4'-
- 25 -methylenebis(cyclohexanol), 4,4'-methylenebis(2-methylcyclohexanol), 4,4'-methylenebis(3-methylcyclohexanol), 3,3'-methylenebis(cyclohexanol), 4,4'-ethylenebis(cyclohexanol), 4,4'-propylenebis(cyclohexanol), 4,4'-butylenebis(cyclohexanol), 4,4'-
- 30 -isopropylidenebis(cyclohexanol), 4,4'-isobutylenebis(cyclohexanol), 4,4'-dihydroxydicyclohexyl, 4,4'-carbonylbis(cyclohexanol), 3,3'-carbonylbis(cyclohexanol), 4,4'-sulfonylbis(cyclohexanol) and 4,4'-oxybis(cyclohexanol); and mixtures of any of the above.

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Preferred for use in the present process are 1,4-butanediol, 1,5-hexanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, the cyclohexanediols including the 1,2-, 1,3-, and 1,4-isomers, and 4,4'-isopropylidenebis(cyclohexanols), and mixtures of the above in accordance with the teachings of the previously mentioned patents.

In respect of the polyol component, its use is optional but, even if employed, it will not be present in proportions which would lower the flexural modulus to values below 150,000 psi (1034 MPa) as measured in accordance with ASTM Test Method-D790. Accordingly, the expedient concentration for the polyol falls in the range of from 0 to 25 parts by weight per 100 parts of total urethane reactants based on (i) organic polyisocyanate, (ii) at least one chain extender and said polyol (iii). If it is selected for incorporation for whatever reason, for example, to increase the impact strength, elongation and tensile strength properties of the resulting plastics, then an advantageous range is from 1 to 15 parts per 100 parts of reactants, and preferably from 1 to 5 parts.

Minimum requirements for the polyol component are a molecular weight of at least 500 and functionality of at least 2. Advantageously, the molecular weight falls within a range of from 500 to 12,000 with a functionality of from 2 to not greater than 6; preferably the molecular weight and functionality are from 500 to 6,000 and from 2 to 4 respectively; most preferably the functionality is from 2 to 3.

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Exemplary of the classes of polyols which can be optionally employed are: polyether polyols, polyester polyols, hydroxy-terminated polycarbonates, hydroxy-terminated polybutadienes, hydroxy-terminated polybutadiene-acrylonitrile copolymers, hydroxy-terminated copolymers of dialkyl siloxane and alkylene oxides such as, for example, ethylene oxide and propylene oxide, and mixtures in which any of the above polyols are employed as major component (greater than 50 percent w/w) with amine-terminated polyethers and amino-terminated polybutadiene-acrylonitrile copolymers.

Illustrative of polyether polyols are polyoxyethylene glycols, polyoxypropylene glycols which, optionally, have been capped with ethylene oxide residues, random and block copolymers of ethylene oxide and propylene oxide, propoxylated tri- and tetrahydric alcohols such as glycerine, trimethylolpropane and pentaerythritol, which propoxylated compounds have been capped with ethylene oxide; polytetramethylene glycol, random and block copolymers of tetrahydrofuran and ethylene oxide and or propylene oxide, and products derived from any of the above reaction with di- or higher functional carboxylic acids or esters derived from said acids in which latter case ester interchange occurs and the esterifying radicals are replaced by polyether polyol radicals. The preferred polyether polyols are random and block copolymers of ethylene and propylene oxide of functionality from 2 to 4, preferably, 2 to 3 and polytetramethylene glycol polymers of functionality greater than or equal to 2.0.

Generally speaking, the overall proportions of the components (i), (ii), and (iii) are such that the

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active hydrogen-containing components (ii) and (iii) balance the isocyanate component (i) so that stoichiometric equivalency of the reactants is maintained. However, for various reasons, it is not always possible nor desirable to meet the 1:1 equivalency. Advantageously, the proportions are such that the overall ratio of isocyanate groups to active hydrogen groups is in the range of from 0.90:1 to 1.10:1, preferably, from 0.95:1 to 1.05:1 and, more preferably, from 0.98:1 to 1.02:1.

It is frequently desirable, but not essential, to include a catalyst in the process. Any of the catalysts conventionally employed in the art to catalyze the reaction of an isocyanate with a reactive hydrogen-containing compound can be employed for this purpose; see, for example, Saunders et al., Polyurethanes, Chemistry and Technology, Part I, Interscience, New York, 1963, pages 228-232; see also Britain et al., J. Applied Polymer Science, 4, 207-211, 1960. Such catalysts include organic and inorganic acid salts of, and organometallic derivatives of, bismuth, lead, tin, iron, antimony, uranium, cadmium, cobalt, thorium, aluminum, mercury, zinc, nickel cerium, molybdenum, vanadium, copper, manganese and zirconium, as well as phosphines and tertiary organic amines. Representative organotin catalysts are stannous octoate, stannous oleate, dibutyltin dioctoate and dibutyltin dilaurate. Representative tertiary organic amine catalysts are triethylamine, triethylenediamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetraethylethylenediamine, N-methylmorpholine, N-ethylmorpholine, N,N,N',N'-tetramethylguanidine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N-dimethylethanolamine and N,N-diethylethanolamine. The amount of catalyst employed

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is generally within the range of from 0.02 to 2.0 percent by weight based on the total weight of the reactants.

5 Included in the process is the one-shot procedure, wherein all the reactants are brought together all at once in the extrusion apparatus, and the prepolymer or quasi-prepolymer techniques. The use of a prepolymer technique would, of course, be limited  
10 primarily to those formulations employing the polyol component (iii) wherein part or all of the polyol is first reacted with isocyanate and the isocyanate prepolymer, then fed to the extrusion apparatus along with the extender. However, the preferred method is the  
15 one-shot reaction.

Additionally, the process can also include various additives such as impact modifiers, fillers and fiber glass; antioxidants, pigments, fire retardants,  
20 plasticizers, reinforcing agents and wax lubricants commonly employed in the art in such compositions. These may be added along with the reactants or at a later stage through a downstream feed port, or at a post  
25 reactor compounding step.

The process in accordance with the present invention is carried out by feeding the above ingredients into a commercial multi-screw extruder which is,  
30 generally speaking, a twin-screw extruder. The screws can be co- or counter-rotating. Preferably, a co-rotating and self-cleaning twin-screw extruder is employed. The general procedures and extrusion equipment described in U.S. Patents 3,642,964 and 3,963,679 can be employed herein except for the novel



exceptions discussed hereinbelow. Generally speaking, the reactive extrusion process is carried out within an overall temperature range of from 150°C to 280°C. That is to say, individual zones may not all be at the same temperatures but their individual values will fall within this range.

The reactants can be measured out using known means such as, for example, gear pumps, membrane or piston pumps for delivery to the extruder feed zone. Figure 1 shows one schematic embodiment of the process wherein (A), (B), and (C) represent three separate reactant feed lines for the isocyanate component, polyol component, and catalyst component respectively. It is not essential that all three lines be utilized. For example, catalyst may be included in the (B) feed line; alternatively, and, if desired, the reactants may be mixed in a suitable mixing head before they are introduced into the extruder. In that case, (A) represents a mixing head which includes all the reactants with catalyst or else the catalyst may be added separately as (B). One of the advantages of the present process is that viscosity build-up of the reaction mixture in the FEED ZONE is not in any way a particular problem. In fact, one of the key features of the present process is that the reaction mixture viscosity should exceed 100,000 cps (100 Pa·s) before reaching the critical SINGLE HIGH SHEAR MIXING ZONE (hereinafter MIXING ZONE). In this regard, the gel time for the reactant systems should be less than about 10 seconds, preferably less than about 6 seconds and FEED ZONE temperatures can fall within a range of from 150°C to 250°C. The FEED ZONE length and conveying screws are in no way critical to the present process and can be

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configured as in the previously mentioned U.S. patents. Actual barrel lengths for the FEED ZONE will be defined by the overall L/D (length/diameter) of the extruder which will be discussed in detail below.

5           Besides the differences in the reaction mix  
viscosities in the FEED ZONES between the present  
process and the prior art cited supra particularly U.S.  
Patent 3,963,679, the limitation of the present MIXING  
10 ZONE to one single zone of high shear mixing is a very  
critical and novel feature which results in polymer  
improvements that otherwise cannot be obtained with the  
hard polyurethanes. Such multiple zones of high shear  
mixing are described in detail in the previously  
15 mentioned patents, particularly the '679 reference.  
Generally speaking, such high shear mixing zones employ  
two series of broad edged multiple kneading elements or  
blocks mounted in intermeshing relationship on the pair  
of parallel mounted screws in the twin-screw extruder in  
20 each zone. The individual kneading elements or blocks  
can be triangular, circular or elliptical as typically  
disclosed in the figures 2 through 7 of the '679 patent.  
The dimensions are such that there is minimal radial  
clearance between the inner surface of the barrel and  
25 the perimeter edges of the blocks. Hence, rotation of  
the screws subjects the reaction mixture to high shear  
forces. Additional mixing and application of high shear  
forces can be imparted, if desired, by mounting  
30 appropriate baffles but more usually reverse pitch  
kneading blocks. Generally speaking, conveying screws  
are present in the same extruder barrel sections which  
contain the zone of kneading blocks.

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What distinguishes the present process is the fact that the high shear mixing is carried out in just a single zone of these multiple kneading elements and not a series of repetitive zones. Advantageously, the actual length of the kneading elements within the single zone will fall within a range of from 50 mm to 240 mm, preferably from 80 to 180, and more preferably from 120 to 180 mm.

In order to provide sufficient shearing forces in the polymer forming mixture, a sufficiently high shear rate or velocity gradient must be achieved. Generally speaking, this is related to the combination of the minimal radial clearances between the barrel (extruder wall) and shearing edges of the blocks referred to above and the speed of screw rotation. Advantageously, this clearance will fall within a range of from 0.05 mm to 0.6 mm, preferably from 0.1 to 0.4 mm. Screw rotation expressed in rotations per minute (r.p.m.) will fall within a range of from 140 to 500 r.p.m., preferably 150 to 300 r.p.m.

Temperatures in the MIXING ZONE will be controlled within a range similar to the FEED ZONE with optionally a slightly higher range, that is to say, from 150°C to 280°C. Capability of cooling this zone should be provided in the event that exotherm could exceed the upper limit of 280°C.

The EXTRUSION ZONE, sometimes called the METERING ZONE, can be configured similarly to the prior art with only conveying screws. Temperatures are advantageously controlled to a range of from 180°C to 280°C. The reacted melt product is simply extruded at

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the end through any desired molding tool or die known to the art such as, for example, slot dies, profile-forming dies and rods.

5           There is no particular limit on overall barrel  
length other than what is dictated by practical con-  
siderations. However, a particularly attractive feature  
of the present process are the short barrel lengths  
which are possible. Advantageously, the L/D ratio can  
10 fall within a range of from 10/1 to 44/1, preferably  
from 15/1 to 25/1, most preferably from 15/1 to 20/1.  
Overall temperature control throughout the above L/D  
ranges, whether it be through heating and/or cooling in  
particular zones, will fall within the previously stated  
15 range of from 150°C to 280°C. Overall residence times in  
the extruder when operating under these L/D,  
temperature, and r.p.m. conditions set forth above will  
fall within a range of from 5 to 45 seconds, preferably  
from 6 to 30 seconds, more preferably from 6 to 25  
20 seconds.

          The extruded polyurethanes can be in finally  
desired shape or else comminuted or pelletized for  
25 further molding or injection molding into desired  
articles. The polymers as obtained need no further  
treatment, having attained their superior physical and  
mechanical properties as set forth in the three patents  
cited supra and already incorporated herein.

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          The following examples describe the manner and  
process of making and using the invention and set forth  
the best mode contemplated by the inventors of carrying

out the invention but are not to be construed as limiting.

Example 1

5       The following experiment sets forth a comparison of two reactive extrusion methods, one in accordance with the invention (run 1) and the other (comparison 1) in accordance with the prior art.

10       A Werner and Pfleiderer ZSK-53 self-cleaning, co-rotating twin-screw extruder was fitted with five barrels of which four had high shear mixing zones. Each of the latter zones were 240 mm in length but only 120  
15 mm of this length was formed of the actual high shear kneading blocks themselves with the remainder given over to conveying screws. Radial clearance between extruder wall and outer diameter of the shearing edges of each kneading block was about 0.2 mm. Screw speed was controlled to 460 r.p.m. Extruder temperatures were controlled by five independent barrel heating or cooling  
20 zones. Feed zone temperature was  $225 \pm 5^\circ\text{C}$ , with extrusion zone being  $215 \pm 5^\circ\text{C}$  and the intermediate zones including the four high shear mixing zones being  
25 190 to  $210^\circ\text{C}$ . A sheeting die, 200 mm width and 3 mm gap was flanged to the end of the extrusion zone.

30       For comparison 1, a mixture in the proportional parts by weight of 100 parts of 1,4-cyclohexanedi-methanol, 0.82 parts of trisnonylphenyl phosphite and 0.69 parts of Irganox 1010 (antioxidant supplied by Ciba Geigy Corp.) was degassed and dehydrated under vacuum at  $99^\circ\text{C}$  for 2 hours. Using a gear pump, this mixture was delivered to the front feed port of the extruder. This means that the length/diameter (L/D) ratio for this feed

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passing through the 2344 mm of length for the five zones of the barrel was 44/1. A second gear pump delivered to the same front feed port 175.2 parts of melted 4,4'-methylenebis(phenyl isocyanate) per 100 parts of the above diol, while a third pump delivered at the same proportional rate 0.33 part of a polyurethane catalyst Femrez UL-22 which is dimethyltindidodecyl mercaptide supplied by Witco Corporation. Gel time of this reacting mixture determined by hand mixing the components rapidly in a beaker was less than 10 seconds. The polymer was extruded onto a metal conveyor belt at 26°C, cooled and diced. At this point the solidified polymer was observed for the formation of bubbles. After drying at 115°C in a dehumidifying hopper dryer with a dew point below -28°C, the pellets were injection molded into test specimens. Their physical properties were determined according to ASTM test procedures with the results set forth in Table I.

Run 1 in accordance with the invention was carried out identically to the above comparison run in every respect except the reactants were fed into a downstream feed port. The second feed port was located in the extruder barrel which was just prior to the last (i.e. fourth) high shear mixing zone. Feeding the reactants at this point shortened the barrel to 919 mm and reduced the L/D to 17.3/1. More importantly, the reaction mixture passed through a single zone of high shear mixing wherein the actual length of kneading blocks was 120 mm.

Comparison of the two extrudates showed run 1 to be essentially clear with the presence of very few minute bubbles, essentially no more than what are to be

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expected in the extrusion of transparent type thermo-  
plastics. Contrastingly, Comparison 1 showed copious  
bubbles in the solidified extrudate. In respect of  
color formation as measured by Yellowness Index, run 1  
was much lower in color compared with comparison 1. As  
for molecular weights and other physical properties, run  
1 appeared to be superior in most respects.

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TABLE I

	Run	Comp. 1	1
	Polymer M.W. <sup>1</sup>	232,432	286,654
5	Flex Modulus, psi x 10 <sup>3</sup> (GPa)	311.3 (2.15)	305.0 (2.1)
	Flex strength, psi (MPa)	14,714 (101.4)	14,898 (102.7)
	Tensile strength, psi (MPa)		
	Yield	11,624 (80.1)	11,634 (80.2)
10	Break	8,634 (59.5)	9,086 (62.6)
	Tensile modulus, psi x 10 <sup>3</sup> (GPa)	293.4 (2.02)	289.2 (1.99)
	Elongation (%)		
	Yield	8.2	8.3
15	Break	34.6	31.0
	HDT <sup>2</sup> (°C)		
	66 psi (455 kPa)	133	135
	264 psi (1820 kPa)	123	123
	Notched Izod <sup>3</sup> ft-lbs/in (J/m) notch		
20	1/8" (3.175 mm) thick sample	1.10 (58.7)	1.24 (66.2)
	1/4" (6.35 mm) thick sample	0.74 (39.5)	1.40 (74.7)
	Yellowness Index <sup>4</sup>	9.05	5.75
25	Bubble Formation <sup>5</sup>	copious bubbles	very few bubbles

Footnotes to TABLE I

<sup>1</sup> Polymer weight average molecular weight determined by gel permeation chromatography using a polystyrene reference as standard.

30 <sup>2</sup> HDT: Heat deflection temperature measured at the specified pressures in accordance with ASTM Test Method D-648.

<sup>3</sup> Notched Izod: Izod impact strength measured on 1/8" and 1/4" (3.175 mm and 6.35 mm) thick samples in accordance with ASTM D256-56.



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4 Yellowness Index: determined using ASTM D-1925 standard at a two degree observer angle using a Pacific Scientific Spectrogard Color System, Silver Spring, Maryland 20910 with the illuminant being simulated average daylight.

5 Bubble Formation: refers to the qualitative visual observation of the extruded polymer for the formation of bubbles; presence of a very few minute bubbles can be tolerated and the polymers classified as essentially a clear plastic, whereas the formation of a copious number of bubbles is not acceptable.

### Example 2

10 Similarly to Example 1, this experiment describes comparison 2 and run 2 reactive extrusions wherein the same apparatus and conditions were employed herein with the exception of different reactant com-  
15 ponents.

The mixture pumped to the first feed port for comparison 2 which ran through the four mixing zones was as follows: a degassed and dehydrated mixture of 100  
20 parts of an 85/15 mole ratio of 1,4-cyclohexane-dimethanol and hydrogenated bisphenol-A, 0.77 parts trisnonylphenyl phosphite, and 0.64 parts of Irganox 1010; 158.35 parts of melted 4,4'-methylenebis(phenyl  
25 isocyanate); and 0.31 part of Fomrez UL-22. For run 2 which ran through only the single zone of high shear mixing, the same three part ingredient mixture was fed into the downstream feed port for the L/D ratio of  
17.3/1.

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The properties of the injection molded samples from the two runs are set forth in Table II. Significantly less gassing in the initial extrudate and lower color for molded run 2 specimens compared to comparison

-24-

2 was observed. Their physical properties were essentially comparable.

TABLE II

	Run	Comp. 2	2
5	Polymer M.W.	203,761	212,193
	Flex Modulus, psi x 10 <sup>3</sup> (GPa)	320.6 (2.21)	311.6 (2.14)
	Flex strength, psi (MPa)	12,918 (89)	12,812 (88)
10	Tensile strength, psi (MPa)		
	Yield	11,887 (82)	11,826 (81.5)
	Break	8,729 (60.2)	8,664 (59.7)
	Tensile modulus, (psi x 10 <sup>3</sup> )	295.8 (2.04)	291.4 (2.01)
	Elongation (%)		
15	Yield	8.3	8.2
	Break	22.1	24.9
	HDT (°C)		
	66 psi (455 kPa)	145	145
20	264 psi (1820 kPa)	135	139
	Notched Izod ft-lbs/in (J/m) notch		
	1/8" (3.175 mm) thick sample	1.15 (61.4)	1.02 (54.4)
	1/4" (6.35 mm) thick sample	0.82 (43.8)	0.93 (49.6)
25	Yellowness Index	8.13	5.64
	Bubble Formation	copious bubbles	very few bubbles

### 30 Example 3

This experiment similar to those above compared the properties of the extrudates and the injection molded samples from comparison 3 and run 3. Using the same extruder configurations and conditions set forth in

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Example 1, the comparison 3 ingredients were fed into the front feed port of the extruder barrel while the same ingredients were fed into the downstream feed port for run 3 with the latter having only the single zone of high shear mixing. The ingredients were as follows:

5 degassed and dehydrated mixture of 100 parts of 1,6-hexanediol, 0.94 part trisnonylphenyl phosphite, and 0.78 part of Irganox 1010; 213.8 part of melted 4,4'-methylenebis(phenyl isocyanate); and 0.19 part of

10 Fomrez UL-22.

The properties of the two product runs are set forth in Table III. The data show significantly less gassing and lower color for run 3 compared with its

15 comparison sample.

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TABLE III

Run	Comp. 3	3
Polymer M.W.	583,000	642,500
5 Tensile strength, psi (MPa)		
Yield	8960 (61.8)	7650 (52.7)
Break	6600 (45.5)	9865 (68)
Tensile modulus, psi x 10 <sup>3</sup> (GPa)	256 (1.77)	273 (1.88)
10 Elongation (%)		
Yield	7	5
Break	27	166
HDT (°C)		
15    66 psi (455 kPa)	88	86
264 psi (1820 kPa)	75	76
Notched Izod ft-lbs/in (J/m) notch		
1/8" (3.175 mm) thick sample	1.747 (93.3)	2.399 (128)
20    1/4" (6.35 mm) thick sample	1.294 (69.1)	1.782 (95.1)
Bubble Formation	COPIOUS BUBBLES	VERY FEW BUBBLES

25 Example 4

This example describes the preparation of a hard thermoplastic polyurethane polymer in accordance with the present invention (run 4) and comparison 4.

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In run 4, a self-cleaning twin-screw Werner and Pfleiderer ZSK-120V was employed with a single zone of high shear mixing at an L/D ratio of 9.5/1 from the feed port and with an overall extruder L/D of 18.8/1. The actual length of kneading blocks in the high shear

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mixing zone was 180 mm. Screw speed was 250 r.p.m. and with about 0.2 mm radial clearance between extruder wall and outer diameter of the shearing edges of each kneading block. Zone temperatures were feed, 188°C; mixing, 177 to 199°C; and extrusion, 230°C.

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The reaction mixture which was metered into the feed port in three streams in the following proportions in parts by weight was as follows: degassed and dehydrated mixture of 43.2 parts of 1,4-cyclohexane-dimethanol, 23.6 parts of 1,6-hexanediol, 10.4 parts of a 650 molecular weight polytetramethylene glycol, 0.52 part of Irganox 1010, and 0.31 part of triphenyl phosphite; 130.79 parts of 4,4-methylenebis(phenyl isocyanate); and 0.10 part of a 50/50 weight mixture of stannous octoate and dioctyl phthalate. The extruded product was fed onto a cool conveyor as described in the previous examples and diced. The extruded material was clear transparent with only a few minute bubbles being detectable. The injection molded product had the following properties set forth in Table IV.

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Comparison 4 was carried out under essentially the same temperature conditions with identical ingredients to run 4 but using a twin-screw Werner and Pfleiderer extruder having an 83 mm diameter, equipped with three zones of high shear mixing and an L/D of 30.7/1.

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A comparison of the two runs shows that run 4 provided a product with much superior molecular weight to the comparison run 4 and a measurably better yellow index and transmission. Notably, this was accomplished

with much less power consumption as compared with comparison 4.

TABLE IV

5	Run	Comp. 4	4
	Polymer M.W.	266,302	359,352
	Tensile Strength, psi (MPa)		
	Yield	10,305	9,896
10	Break	7,867	7,703
	Tensile Modulus, psi $\times 10^3$ (GPa)	274 (1.89)	274.8 (1.9)
	Elongation (%)		
	Yield	6.4	5.7
15	Break	42	45
	Yellowness Index	5.52	4.74
	Transmission at 380 nm <sup>1</sup>	58.05%	61.97%

20 Footnote to Table IV

1 Light transmittance in percent measured on injection molded disk measuring 2 inches (51 mm) diameter  $\times$  1/8" (3.2 mm) thick at 380 nanometers using Pacific Scientific Spectrogard Color Systems, Silver Spring, Maryland, 20910.

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1. A reactive extrusion process for the continuous preparation of a polyurethane having a  $T_g$  greater than  $80^\circ\text{C}$  from a reaction mixture comprising a polyisocyanate and at least one polyol component by passing said reaction mixture through a twin-screw extruder having besides the feed zone, zones of high shear mixing and a metering zone, characterized by  
5 limiting the high shear mixing to a single zone.
2. A process according to Claim 1 wherein in said single zone of high shear mixing the radial clearance between the outer diameter of the shearing edges  
10 and the extruder wall is from 0.05 to 0.6 mm and the rotation of the screw is from 140 to 500 r.p.m.
3. A process according to Claim 1 wherein the  
15 reaction mixture is passed through said single zone of high shear mixing after having reached a viscosity greater than 100,000 cps (100 Pa·s).
4. A process according to Claim 1 wherein  
20 said reaction mixture comprises (i) an organic polyisocyanate, (ii) at least one chain extender, and (iii) 0 to 25 parts by weight per 100 parts of total polyurethane reactants of a polyol having a  
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functionality of at least 2 and molecular weight of at least 500.

5 5. A process according to Claim 1 wherein the temperature of reactive extrusion is carried out at a temperature of from 150°C to 280°C.

10 6. A process according to Claim 1 wherein the proportions of said polyisocyanate and at least one polyol are such that the ratio of equivalents of isocyanate to hydroxyl falls within a range of from 0.95 to 1.05.

15 7. A reactive extrusion process for the continuous preparation of a thermoplastic polyurethane having a T<sub>g</sub> greater than 80°C which process comprises:

(A) adding to the feed zone of co-rotating twin-screw extruder a reaction mixture comprising:

- 20 (i) an aromatic diisocyanate;  
(ii) at least one diol extender having a molecular weight of from 60 to 400;  
(iii) 0 to 25 parts by weight per 100 parts of  
25 total polyurethane reactants of a polyol having a functionality of from 2 to 3 and a molecular weight of from 500 to 6,000; and  
(iv) a urethane catalyst, wherein the proportions of said diisocyanate (i) and components (ii) and (iii) are such that the ratio of  
30 equivalents of isocyanate to hydroxyl is from 0.95 to 1.05;

(B) mixing and homogenizing said reaction mixture after having reached a viscosity greater than 100,000 cps (100 Pa·s) in a single zone of high shear mixing at



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a temperature of from 150°C to 280°C and wherein the radial clearance between the outer diameter of the shearing edges and the extruder wall is from 0.05 to 0.6 mm and the screw rotation is from 140 to 500 r.p.m.; and

- 5 (C) removing the resulting polyurethane via a metering and shaping zone.

8. A process according to Claim 7 wherein said (ii) comprises 1,4-cyclohexanedimethanol, a mixture  
10 of 1,4-cyclohexanedimethanol and hydrogenated bisphenol A or 1,6-hexanediol.

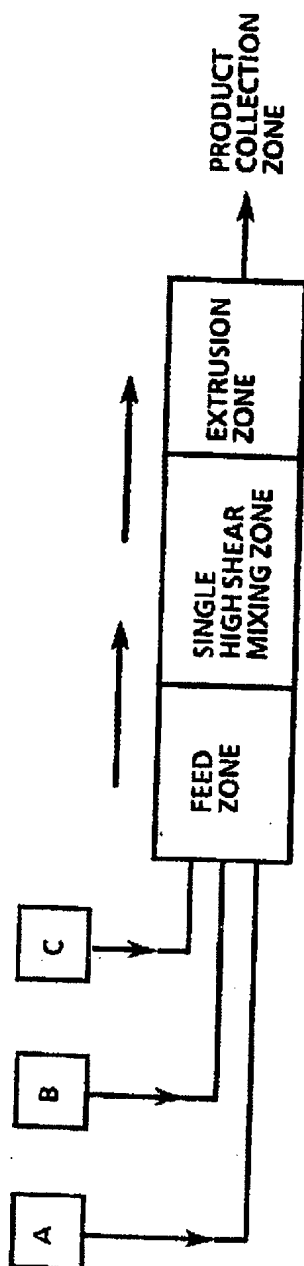
9. A process according to Claim 7 wherein said aromatic diisocyanate is 4,4'-methylenebis(phenyl  
15 isocyanate) and said polyol is present in the proportions of from 1 to 15 parts.

10. A process according to Claim 9 wherein  
20 said diol extender comprises a mixture of 1,4-cyclohexanedimethanol and 1,6-hexanediol and said polyol is a polytetramethylene glycol of molecular weight from 650 to 1,000.

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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/02869

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>1</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> : C 08 G 18/08, C 08 G 18/32		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>2</sup>		
Classification System	Classification Symbols	
IPC <sup>5</sup>	C 08 G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>3</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>4</sup></b>		
Category <sup>5</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	DE, A, 2447368 (BASF) 8 April 1976 see claim; page 3, paragraph 5 - page 4, paragraph 4; example 1  --	1-7
Y	DE, C, 895058 (BASF) 19 November 1953 see claim; example 3  --	1-7
X	US, A, 3642964 (K.W. RAUSCH et al.) 15 February 1972 see claims 1,7; column 4, lines 29-70; column 5, lines 22-33; column 7, lines 27-39; column 9, lines 51-71 (cited in the application)  --	1-7
<p><sup>1</sup> Special categories of cited documents: <sup>14</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
11th October 1990	16. 11. 90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 H. Ballesteros	

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US, A, 4822827 (H.W. BONK et al.) 18 April 1989 see claims 1,7,8,11,16,17,23,; column 3, lines 6-17,53-68 (cited in the application)  --	1,8-10
A	US, A, 3963679 (M. ULLRICH et al.) 15 June 1976 see claims 1-3; column 9, lines 43-53 (cited in the application)  --	1
A	EP, A, 0254250 (AUSIMONT S.p.A.) 27 January 1988 see claims 1,5,7-9; page 4, lines 5-19; page 5, lines 11-25  -----	1

Form PCT/ISA 210(extra sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9002869  
SA 38251

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/11/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A- 2447368	08-04-76	None	
DE-C- 895058		None	
US-A- 3642964	15-02-72	BE-A- 759829	03-06-71
		DE-A, B 2059570	09-06-71
		FR-A- 2072814	24-09-71
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US-A- 4822827	18-04-89	AU-A- 2641188	22-06-89
		EP-A- 0320946	21-06-89
		JP-A- 1259023	16-10-89
US-A- 3963679	15-06-76	None	
EP-A- 0254250	27-01-88	JP-A- 63066218	24-03-88
		US-A, B 4769435	06-09-88

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